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PMR Polyimides—Review and Update

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ABSTRACT

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Fiber reinforced PMR polyimides are finding increased acceptance as engineering materials for high performance structural applications. Prepreg materials based on this novel class of highly processable, high temperature resistant polyimides which were first developed at the NASA Lewis Research Center are commercially available and the PMR concept has been adopted by other investigators. This paper reviews the current status of first and second generation PMR polyimides. Emphasis is given to the chemistry, processing and applications of the first generation material known as PMR-15.

1. INTRODUCTION

Until recently the application of polymer matrix composite materials has been limited to structural components fabricated from fiber reinforced epoxy resins. Composites made with epoxy resins can be easily processed at relatively low pressures and temperatures using a variety of techniques, but their application is limited to temperatures not exceeding 350°F. In an effort to extend the upper use-temperature limit of composite materials to 600°F, polymer

chemists have synthesized a variety of condensation-type matrix resins during the last two decades. However, the severe processing requirements of early technology high temperature polymers made it difficult and impractical to fabricate high quality structural components.

Studies conducted at the NASA Lewis Research Center led to the development of a novel class of addition-type polyimides known as PMR polyimides for in situ Polymerization of Monomer Reactants. These polyimides can be processed into high quality, essentially void-free components by either compression or autoclave molding techniques, and thus are making it possible to realize much of the potential of high temperature polymer matrix composites.

The purpose of this paper is to review and up-date the current status of PMR polyimides.

2. DISCUSSION

2.1 PMR Polyimide Matrix Resins

The PMR approach for preparing fiber-reinforced addition-type polyimides was developed by investigators at NASA Lewis Research Center in 1972. (1-4)

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In this approach a dialkyl ester of an aromatic tetracarboxylic acid, an aromatic diamine, and a monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) are dissolved in a low boiling point alkyl alcohol. The solution is used to impregnate the reinforcing fibers. The number of moles of each reactant is governed by the ratio $n:(n+1):2$, where n , $(n+1)$, and 2 are the number of moles of the dialkyl ester of the aromatic tetracarboxylic acid, the aromatic diamine, and NE, respectively. In the temperature range of 250-450°F the monomers undergo in situ cyclodehydration to form a norbornenyl-endcapped, low molecular weight imide prepolymer. Addition polymerization of the norbornenyl endcaps occurs at temperatures of 525-660°F without the evolution of volatile reaction byproducts, making it possible to fabricate composites having void contents of less than one percent.

In the initial study (1) which established the feasibility of the PMR approach, it was noted that composites fabricated from Hercules HTS graphite fibers and 50 weight percent monomer solutions of the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), 4,4'-methylenedianiline (MDA), and NE exhibited a greater level of thermo-oxidative stability than composites prepared from monomer solutions of the dimethyl ester of pyromellitic acid, MDA, and NE. This unexpected finding was confirmed in a subsequent study (5) which investigated the effect of eight different aromatic diamines on composite properties. The best overall balance of processing characteristics, composite thermo-mechanical and physical properties, and 600°F thermo-oxidative stability was provided by a monomer combination of BTDE:MDA:NE in a molar ratio of 2.087:3.087:2, corresponding to a formulated molecular weight (FMW) of 1500. The FMW is considered to be the average molecular weight of

imidized prepolymer that would have been formed if an amide-acid prepolymer had been synthesized and then imidized. The equation for the FMW of a PMR polyimide prepared from n moles of BTDE, $(n+1)$ moles of MDA, and 2 moles of NE is:

$$\text{FMW} = n\text{MW}_{\text{BTDE}} + (n+1)\text{MW}_{\text{MDA}} + 2\text{MW}_{\text{NE}} - 2(n+1)[\text{MW}_{\text{H}_2\text{O}} + \text{MW}_{\text{CH}_3\text{OH}}]$$

where MW denotes the molecular weights of the monomer reactants and byproducts. The PMR resins prepared from BTDE are referred to as "first generation" materials. It is now common practice to denote the stoichiometry of a PMR resin by dividing the FMW by 100. Thus, the first generation PMR matrix resin prepared from BTDE, MDA, and NE having an FMW of 1500 is now widely known as PMR-15. Prepreg materials prepared from the PMR-15 resin are commercially available from several major prepreg suppliers. The structures of the monomers used in PMR-15 are shown in Table 1.

These early studies (1,5) clearly indicated the versatility of the PMR approach. By varying the chemical composition of the monomers or the monomer stoichiometry, PMR matrix resins having a broad range of processing characteristics and properties can be readily synthesized. A modified PMR-15, called LARC-160, has been developed by substituting an aromatic polyamine for MDA. (6) Other studies (7) showed the potential of the PMR approach for "tailor making" PMR resins with specific properties. Figure 1 shows the effect of varying the FMW on resin flow for HTS graphite/PMR-15 composites. Significantly higher resin flow could be achieved by decreasing the FMW. However, the compositions having increased resin flow exhibited a decrease in thermo-oxidative stability at 550°F.

Partial or total replacement of BTDE with the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-

bis(phthalic acid) (HFDE) significantly improved the thermo-oxidative stability of "first generation" PMR resins.⁽⁸⁾ The HFDE-PMR compositions are referred to "second generation" materials to distinguish them from the "first generation" BTDE-PMR materials. However, the glass transition temperature (T_g) and initial 600°F mechanical properties of "second generation" HFDE/MDA/NE PMR polyimide composites were considerably lower than the corresponding properties of the "first generation" BTDE/MDA/NE PMR composites. Partial substitution of tetramines for the diamine MDA in first or second generation PMR resins increased the T_g of the composites above 600°F.⁽⁹⁾ An increased T_g was also achieved by replacement of MDA in second generation PMR with p-phenylenediamine (PPDA).⁽¹⁰⁾ Graphite fiber reinforced composites prepared from monomer solutions of HFDE, PPDA, and NE at an FMW of 1267 ($n=1.67$), designated as PMR-II, exhibited significantly improved thermo-oxidative stability and retention of mechanical properties at 600°F compared to PMR-15 composites.⁽¹⁰⁾ The interlaminar shear strength of PMR-II ($n=1.67$) and PMR-13 (a "first generation" resin with $n=1.67$, containing the same number of imide rings) are compared in figure 2. PMR-II has not been widely accepted as a matrix material because of the lack of a commercial source for the dianhydride of HFDE.

→ The cure mechanism of PMR-15 is generally accepted to proceed via the reverse Diels-Alder reaction of the norbornenyl end-groups to generate maleic end-groups and cyclopentadiene.⁽¹¹⁾ The maleic groups then proceed to copolymerize with the double bonds on cyclopentadiene and unreacted norbornenyl groups to produce a cross-linked structure without the evolution of void-producing volatile materials. Differential scanning calorimetry studies have shown the presence of 4 thermal transitions

which occur during the cure of a PMR polyimide.⁽¹²⁾ The first, second, and third transitions are endothermic and are related to the following: (1) melting of the monomer reactant mixture below 212°F, (2) in situ reaction of the monomers at 284°F, and (3) melting of the norbornenyl terminated prepolymers in the range of 350 to 490°F, referred to as the "melt flow" temperature range. The fourth transition, centered near 650°F and exothermic, results from the addition crosslinking reaction. The excellent processing characteristics of PMR polyimides can be attributed to the presence of these chemically distinct and widely separated thermal transitions.⁽¹³⁾

High pressure (compression) and low pressure (autoclave) molding cycles have been developed for fabrication of fiber and particulate reinforced PMR composites. Although the peak crosslinking exotherm is centered at about 650°F, nearly all of the processes developed use a maximum cure temperature of 600°F. A cure time of two hours followed by a free standing postcure in air at 600°F for 16 hours is also normally employed. Compression molding cycles generally employ high heating rates (10 to 20°F/min.) and pressures in the range of 500 to 1000 psi. Vacuum bag autoclave processes at low heating rates (3 to 6 °F/min.) and pressures of 200 psi have been successfully used to fabricate void-free composites.⁽¹⁴⁾

Studies have shown that the processing characteristics and properties of PMR-15 composites are adversely affected by the presence of higher esters (tri and tetra-esters of 3,3',4,4'-benzophenonetetracarboxylic dianhydride) in the monomer reactant solution.⁽¹⁵⁾ The higher esters are believed to be responsible for increased void content and lower thermo-mechanical properties. Recently, however, it has been

shown that by properly adjusting the processing parameters high quality composites can be fabricated from PMR-15 solutions containing as much as 20 weight percent of the higher esters.⁽¹⁶⁾

Many studies have been conducted to determine the effects of various hostile environments on the physical and mechanical properties of PMR-15 composites.⁽¹⁷⁾ Glass, graphite,⁽¹⁸⁻²⁰⁾ and Kevlar⁽²¹⁾ PMR-15 composites have been investigated. Figure 3 shows the excellent 600°F interlaminar shear strength retention characteristics of PMR-15 composites made with four different graphite fibers.⁽¹⁹⁾ The difference in strength levels between the Celanese Celion 6000 composites and the three other composites was attributed to differences in fiber surface morphologies.⁽¹⁹⁾

Resin/fiber thermo-oxidative interactions resulting from the presence of inorganic impurities in the graphite fiber have been shown to play a dominant role in determining the useful lifetime of PMR-15 and PMR-II composites at 600°F.⁽²²⁾ A recent study has shown that the major contributor to composite weight loss during 600°F exposure in air of PMR-15 composites is degradation of MDA.⁽²³⁾ Figure 4 shows the overall resin and individual resin component weight losses in a Celion 6000/PMR-15 composite as a function of 600°F air exposure time.⁽²³⁾ The higher weight loss of the MDA component is clearly evident. The figure also shows the stability of the BTDA (3,3',4,4'-benzophenonetetracarboxylic dianhydride) component and the marked increase in the degradation of the norbornenyl crosslinker after about 1200 to 1500 hours of air exposure at 600°F. The weight loss behavior of the crosslinker correlates with the 600°F performance of PMR-15 composites. Excellent retention of composite mechanical properties and comparatively low composite weight loss are generally observed

for 600°F exposure in air up to about 1500 hours. Thus, it would appear that the 600°F thermo-oxidative stability of the norbornenyl crosslinker determines the useful lifetime of PMR-15 composites at 600°F. However, in a recent study it was found that the addition of low levels (4 and 9 mole percent) of a monofunctional norbornenyl crosslinker to PMR-15 increased the composite thermo-oxidative stability and resin flow during composite processing.⁽²⁴⁾ Although the modified PMR-15 composites exhibited lower initial properties at 600°F than unmodified PMR-15 composites, the addition of small quantities of a monofunctional norbornenyl crosslinker to PMR-15 to increase the 600°F thermo-oxidative stability appears to be a promising approach. At the present time, however, the composition of PMR-15 remains unchanged from the original composition developed in the early seventies.

2.2 Applications

One of the most rewarding aspects of the PMR polyimide development has been the successful demonstration of PMR-15 polyimide composite materials as viable engineering materials. Prepregs, molding compounds and even adhesives based on PMR-15 have been commercially available from the major suppliers of composite materials since the mid seventies. Because of their commercial availability, processability, and excellent retention of properties at elevated temperatures, PMR-15 composites have been used to fabricate a variety of structural components. These components range from small compression molded bearings to large autoclave molded aircraft engine cowls and ducts. Processing technology and baseline materials data are being developed for the application of PMR-15 composites in aircraft engines, space structures, and weapon systems. Some representative applications of PMR-15 composites are listed

in table 2. None of the components listed in the table, except the ion engine beam shield, are applications in the sense that the components are currently being produced or designated as the bill-of-materials. However, several of the components listed in table 2 are scheduled for production introduction in the near future. A brief discussion of each of the components listed in table 2 follows.

The blade illustrated in figure 5 was the first structural component fabricated with a PMR-15 composite material. The reinforcement is HTS graphite fiber. The blade design was conceived by Pratt and Whitney Aircraft (PWA) for an ultra-high speed fan stage.⁽²⁵⁾ Blade tooling and fabrication were performed by TRW Equipment.⁽²⁶⁾ The blade span is 11 in. and the chord is 8 in. The blade thickness ranges from about 0.5 in. just above the midpoint of the wedge shaped root to 0.022 in. at the leading edge. At its thickest section the composite structure consists of 77 plies of material arranged in varying fiber orientation. The "line of demarkation" visible in figure 5 at approximately one-third the blade-span from the blade-tip resulted from a required change in fiber orientation from 40° in the lower region to 75° in the upper region to meet torsional stiffness requirements. Ultrasonic and radiographic examination of the compression molded blades indicated that they were defect free. Although some minor internal defects were induced in the blades during low cycle and high cycle fatigue testing, the successful fabrication of these highly complex blades established the credibility of PMR-15 as a processable matrix resin.

Figure 6 shows the inner cowl installed on an experimental engine, called QCSEE for a Quiet Clean Short-Haul Experimental Engine, developed by General Electric (GE) under contract with

NASA Lewis.⁽²⁷⁾ The cowl defines the inner boundary of the fan air flowpath from the fan frame to the engine core nozzle. The cowl was autoclave fabricated by GE from PMR-15 and Union Carbide's T300 graphite fabric. The cowl has a maximum diameter of about 36 in. and is primarily of honeycomb sandwich construction. Hexcel's HRH327 fiberglass polyimide honeycomb was used as the core material. The honeycomb core was bonded to the inner surface of the premolded outer skin with duPont's NR150B2G adhesive. The inner skin was then co-cured and bonded with NR150B2G to the core surface of the honeycomb core/outer skin assembly. Complete details about the cowl fabrication process are given in reference 28. The cowl was installed on the QCSEE engine and did not exhibit any degradation after more than 300 hours of ground engine testing. The maximum temperature experienced by the cowl during testing was 500°F.⁽²⁹⁾ The successful autoclave fabrication and ground engine test results of the QCSEE inner cowl established the feasibility of using PMR-15 composite materials for large engine static structures.

Under a jointly sponsored Navy/NASA Lewis program (NAS3-21854) GE is developing a T300 graphite fabric/PMR-15 composite outer duct to replace the titanium duct presently used on the F404 engine for the Navy's F18 strike fighter. The titanium duct is a sophisticated part made by forming and machining titanium plates followed by chem milling to reduce weight. A preliminary cost-benefit study indicated that significant cost and weight savings⁽³⁰⁾ could be achieved by replacing the titanium duct with a composite duct. The F404 composite outer duct differs from the QCSEE inner cowl in several important respects. The F404 duct is a monolithic composite structure, needs to withstand fairly high loads and, perhaps most importantly, the F404 duct is

to be a production component and not a "one-of-a-kind" demonstration component. A full-scale composite duct (38 in. diameter by 65 in. length by 0.080 in. wall thickness) has been autoclave fabricated. The overall duct fabrication process consists of many operations. The sequence of the major operations is as follows: (1) autoclave fabrication of the composite shell, (2) ultrasonic inspection, (3) adhesive bonding of T300 fabric/PMR-15 ply buildups to the shell using PMR-15 as the adhesive, (4) drilling of the buildups and cutting of the shell into two halves and (5) attachment of the split line stiffeners and titanium end-flanges. Figure 7 shows a photograph of the completed outer duct. The duct was installed on an F404 engine (figure 8) and successfully withstood 300 accelerated mission test cycles. The T300/PMR-15 composite outer duct is tentatively scheduled for production introduction in 1985.

Figure 9 shows a full-scale composite forward inner duct fabricated by GE for their F101 DFE (derivative fighter engine). The approximate dimensions of the duct which was autoclave fabricated from T300 graphite fabric/PMR-15 are 40 in. diameter by 15 in. length by 0.060 in. wall thickness. Engine testing demonstrated that the composite duct was fully functional and met engine performance requirements. The T300/PMR-15 composite inner duct is currently scheduled for production introduction in 1985.

The current bill-of-materials inlet particle separator swirl frame on GE's T700 engine is an all metal part that involves machining, shape-forming, welding, and brazing operations. Design studies conducted under U. S. Army contract number DDAK51-79-C-0018 indicated that the fabrication of a metal/composite swirl frame could result in a cost and weight savings of about 30 percent. Figure 10 shows a schematic diagram of a section of the metal/composite swirl frame

that was fabricated from 410 stainless steel and various kinds of PMR-15 composite materials. The outer casing uses stainless steel in the flow path area to meet anti-icing temperature requirements and T300 and glass fabric/PMR-15 hybrid composite to meet structural requirements. The T300/glass hybrid composite was selected on the basis of both cost and structural considerations. An aluminum coated glass fabric PMR-15 composite material is utilized in the inner hub flowpath to meet heat transfer requirements for anti-icing. The glass fabric/PMR-15 composite utilized for the front-edge and front-inner surfaces was selected because of cost as well as temperature considerations. A full-scale (O.D. \approx 20 in.) metal/composite swirl frame has been subjected to sand erosion and ice ball impact tests. The metal/composite swirl frame provided improved particle separation and successfully met the impact test requirements. Fabrication feasibility has been demonstrated and if the metal/composite swirl frame successfully meets all of the performance requirements, the metal/composite T700 swirl frame will be introduced into production in 1985.

Figure 11 shows a photograph of a DC-9. The inserts schematically depict the design of the presently used metal reverser stang fairing and a composite redesigned fairing developed by Douglas Aircraft Company under the NASA Lewis Engine Component Improvement Program.⁽³¹⁾ Studies had shown that a redesigned fairing provided an opportunity to reduce baseline drag and would result in reduced fuel consumption. The fairing serves as the aft enclosure for the thrust reverser actuator system on the nacelle of the JT8D and is subjected to an exhaust temperature of 5000°F during thrust reversal. A Kevlar fabric/PMR-15 composite fairing has been autoclave fabricated and flight-tested. Compared to the metal component, the

composite fairing resulted in a one percent airplane drag reduction (1/2 percent had been anticipated) and a 40 percent reduction in component weight.

Figure 12 is a schematic showing "committed" and "possible" applications of graphite/PMR-15 composite materials on the PW1120 turbojet currently being developed by Pratt and Whitney Aircraft/Government Products Division (PWA/GPD). A committed application is an application for which a metal back-up component is not being developed. The only committed applications for graphite/PMR-15 composites at this time are the external nozzle flaps and the airframe interface ring. PWA/GPD is in the process of completing its assessment of the various "possible" applications and anticipates that many of these will also become "committed", if engine test schedules can be met. The PW1120 engine is currently scheduled for production deliveries in 1986. Graphite/PMR-15 external nozzle flaps are also being developed by PWA/GPD for its PW1130 turbofan engine. Prepregs made from T300 or Celion 3000 uniweave fabrics and PMR-15 are being evaluated for fabrication of the nozzle flaps used on both the PW1120 and PW1130 engines.

The CASTS (Composites for Advanced Transportation Systems) program was undertaken by NASA Langley in 1975 to develop graphite/polyimide composites for application to future aerospace vehicles. As part of the CASTS Program, Boeing Aerospace Company developed manufacturing processes for fabrication of graphite/PMR-15 structural elements and demonstrated their structural integrity at temperatures up to 600°F.⁽³²⁾ The structural elements consisted of flat panels, corrugated stiffeners, I-beams, hat stiffeners, honeycomb panels and chopped fiber moldings. A section (30 in. wide x 80 in. long x 22 in. tapered to 6 in. thick) of a simulated shuttle orbiter aft

body flap (full-scale, 7 x 21 ft.) was successfully fabricated. Thus, demonstrating that the manufacturing processes which were developed for structural elements could be adapted to large scale airframe hardware.

Figure 13 shows a mercury ion thruster for an auxiliary propulsion system being built by Hughes Space and Communications Group under contract to NASA Lewis. The ion propulsion system is scheduled for launch and testing on a future shuttle flight. The thruster is equipped with a glass fabric/PMR-15 composite beam shield to protect the solar arrays and sensitive instrumentation on the spacecraft from ion-beam damage. The composite shield (approximate dimensions: 10 in. diameter by 8 in. length x 0.040 in. thickness) was selected over tantalum and titanium because of weight and structural considerations. The feasibility of using a glass fabric/PMR-15 composite shield was demonstrated by in-house fabrication and testing of full-scale beam shields.

3. CONCLUDING REMARKS

The in situ polymerization of monomer reactants (PMR) approach has been demonstrated to be a powerful approach for solving many of the processing difficulties associated with the use of high temperature resistant polymers as matrix resins in high performance composites. PMR-15, the PMR polyimide discovered in the early seventies, provides the best overall balance of processing characteristics and elevated temperature properties. The excellent properties and commercial availability of composite materials based on PMR-15 have led to their acceptance as viable engineering materials. PMR-15 composites are currently being used to produce a variety of high quality structural components. Increased use of these materials is anticipated in the future.

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Table 1. - MONOMERS USED FOR PMR-15 POLYIMIDE

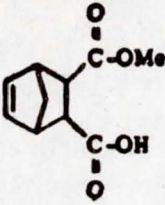
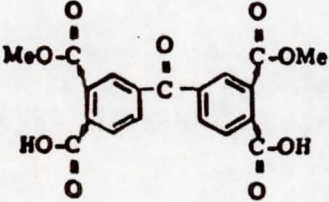
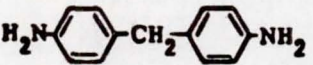
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	4,4'-METHYLENEDIANILINE	MDA

Table 2. - APPLICATIONS OF PMR-15 COMPOSITES

COMPONENT	AGENCY	CONTRACTOR
ULTRA-HIGH TIP SPEED FAN BLADES	NASA-LeRC	PWA/TRW
QCSEE INNER COWL	NASA-LeRC	GE
F404 OUTER DUCT	NAVY/NASA-LeRC	GE
F101 DFE INNER DUCT	AIR FORCE	GE
T700 SWIRL FRAME	ARMY	GE
JT8D REVERSER STANG FAIRING	NASA-LeRC	MCDONNELL-DOUGLAS
EXTERNAL NOZZLE FLAPS		
PW1120	—	PWA ^a
PW1130	AIR FORCE	PWA
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ION THRUSTER BEAM SHIELD	NASA-LeRC	HUGHES

^a COMPANY FUNDED

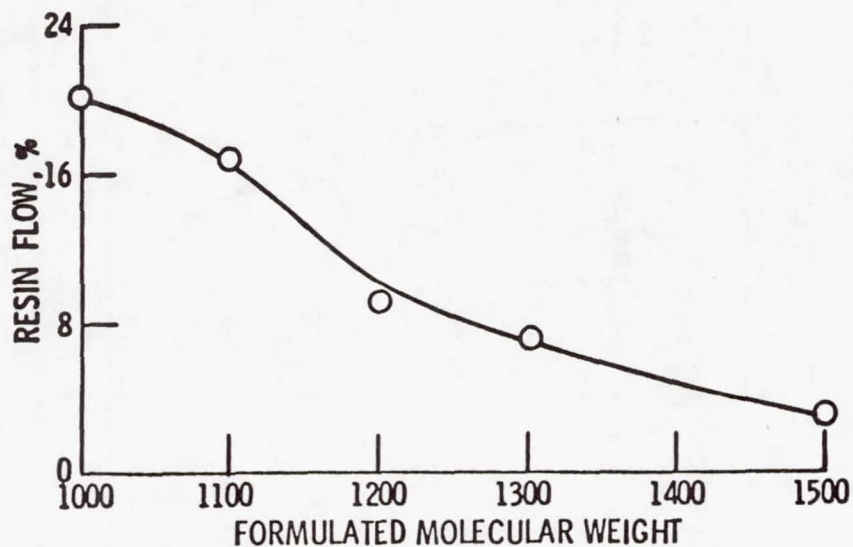


Figure 1. - Resin flow of HTS graphite/PMR composites (Resin flow is based on weight of resin flash formed during molding).

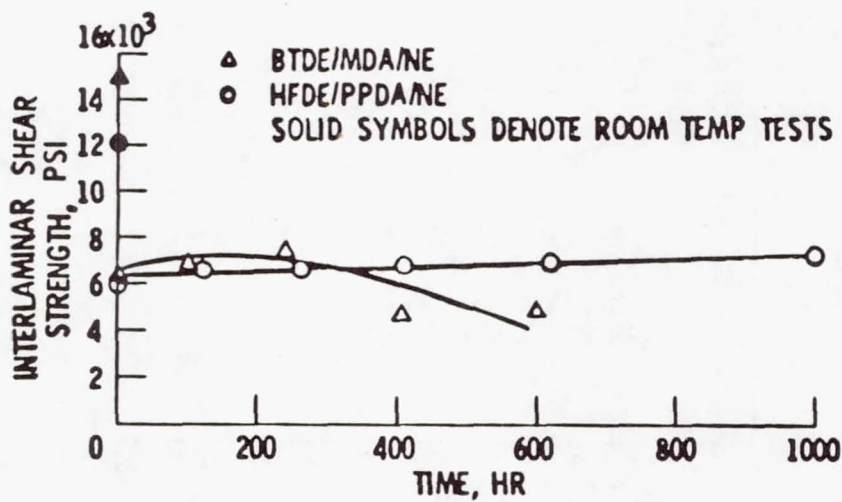


Figure 2. - Interlaminar shear strength of HTS graphite fiber/PMR polyimide ($n = 1.67$) composites exposed and tested at 600°F.

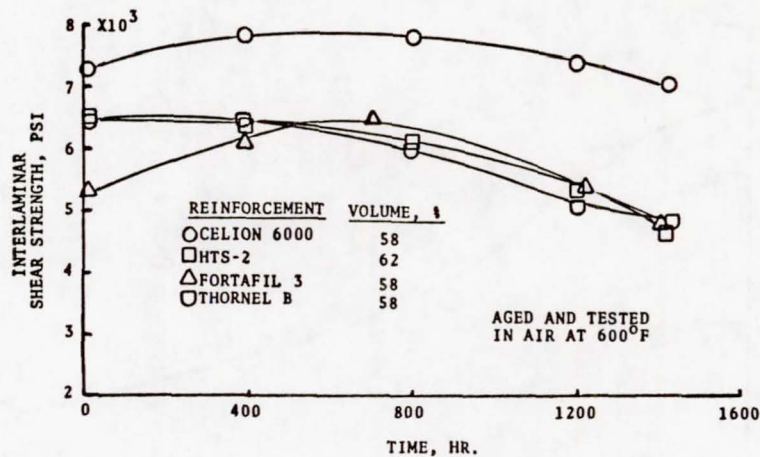


Figure 3. - Interlaminar shear strength of graphite fiber reinforced PMR-15 composites.

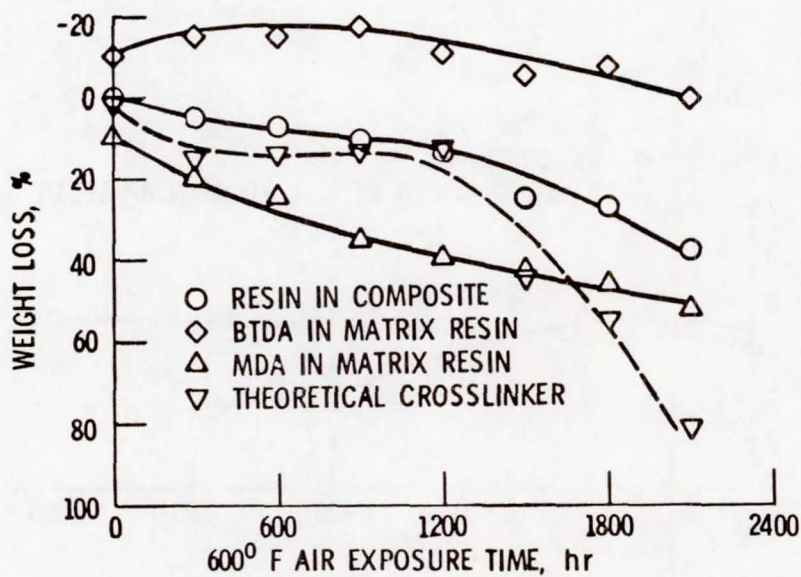


Figure 4. - Component weight losses in Celion 6000/PMR-15 composite.

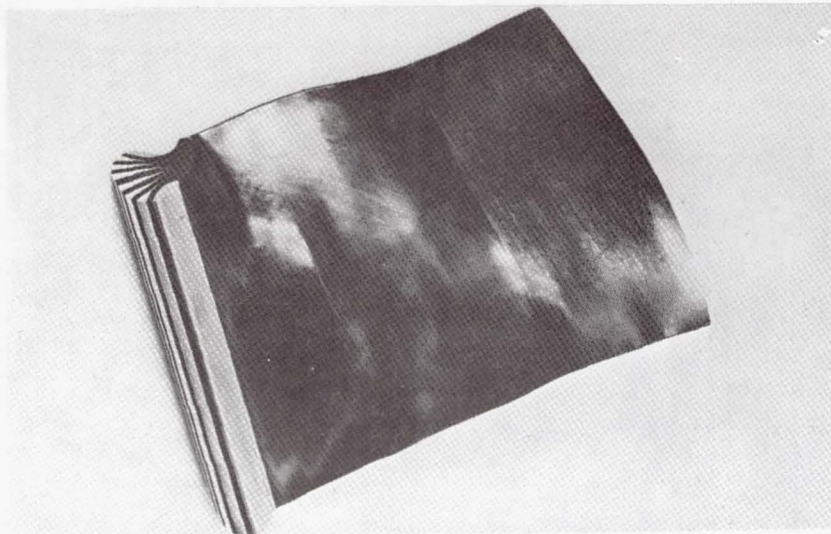


Figure 5. - Graphite fiber/PMR-15 polyimide fan blade (span, chord and thickness = 11, 8 and 0.5 inches, respectively).

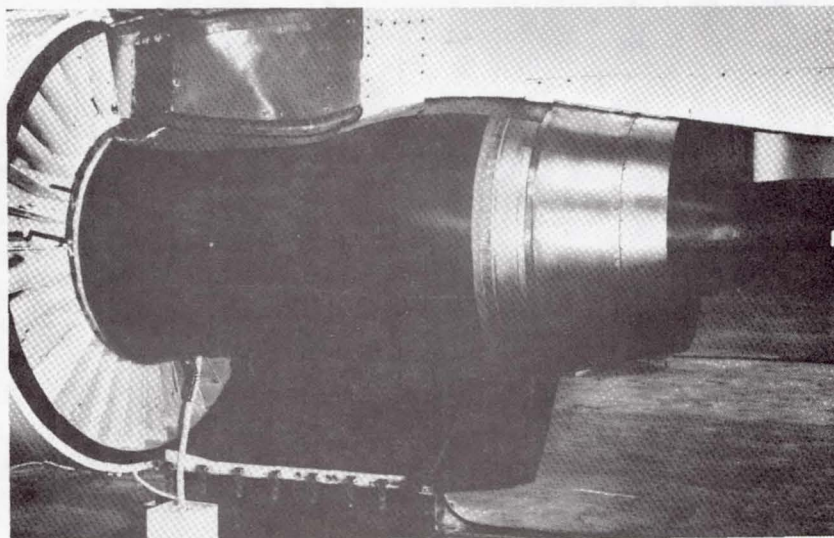


Figure 6. - Graphite fiber/PMR-15 polyimide inner cowl installed on QCSEE engine.

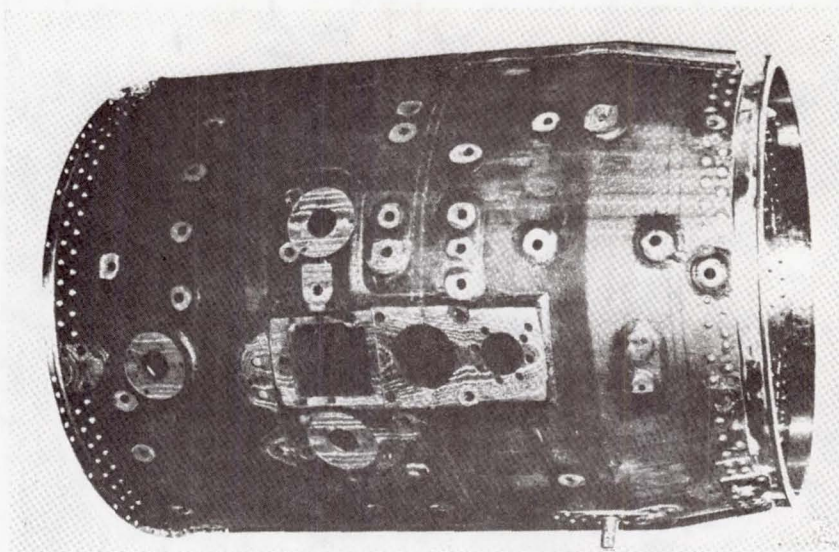


Figure 7. - Graphite fiber/PMR-15 outer duct after final machining.

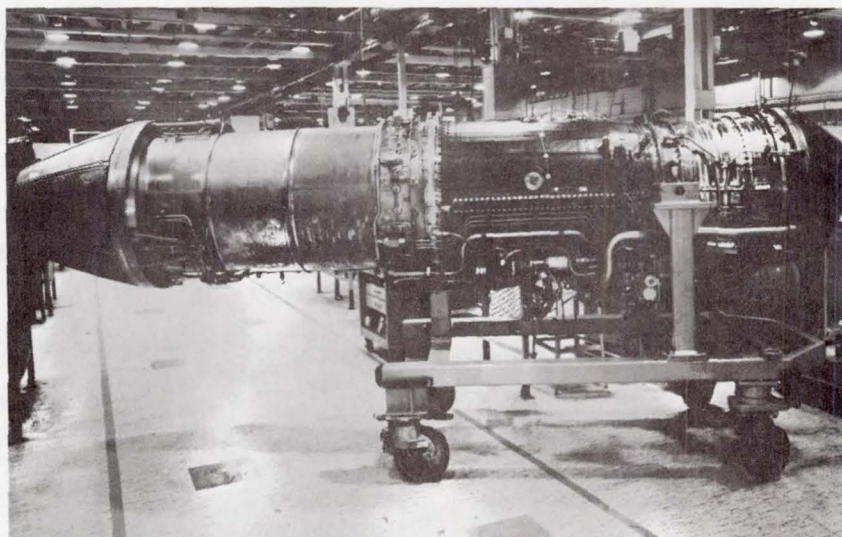


Figure 8. - Graphite fiber/PMR-15 outer duct installed on an F404 engine (composite duct located directly above carriage).

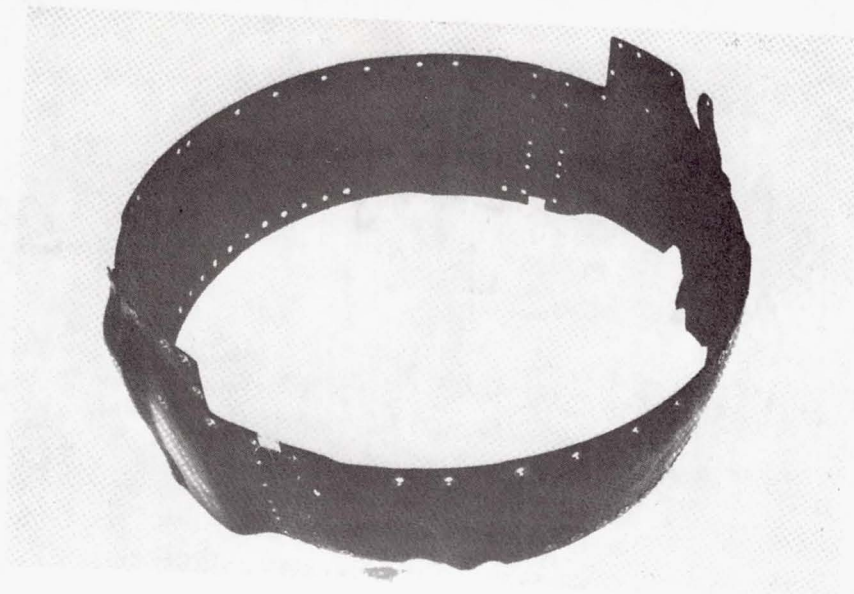


Figure 9. - Graphite fiber/PMR-15 F101 DFE inner duct (Diameter = 40 in., length = 15 in., and thickness = 0.060 in.).

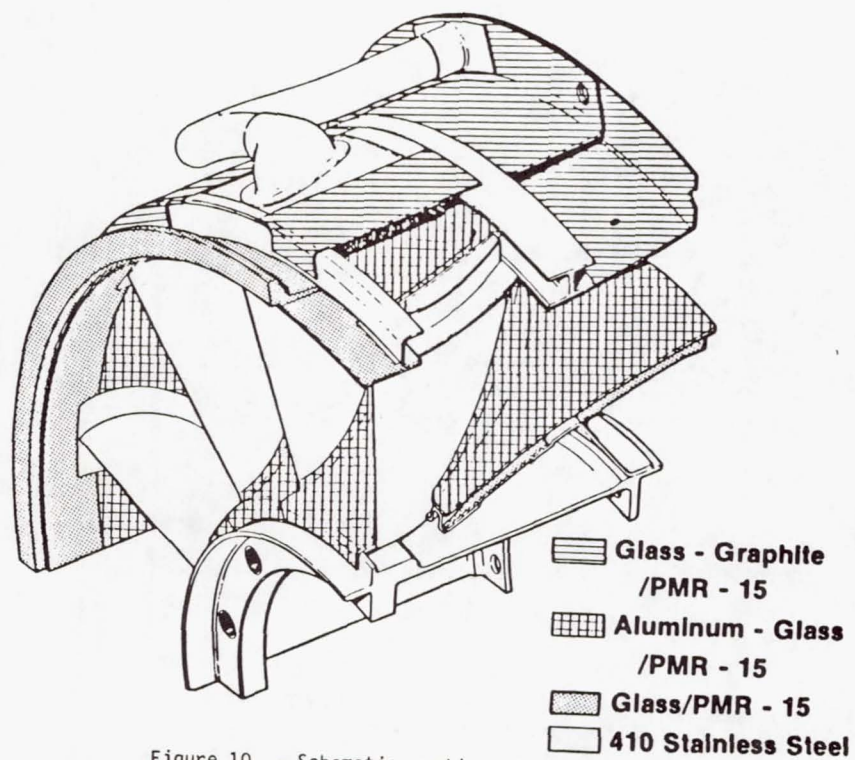


Figure 10. - Schematic section of the T700 PMR-15 composite swirl frame (O. D. = 20 in.).

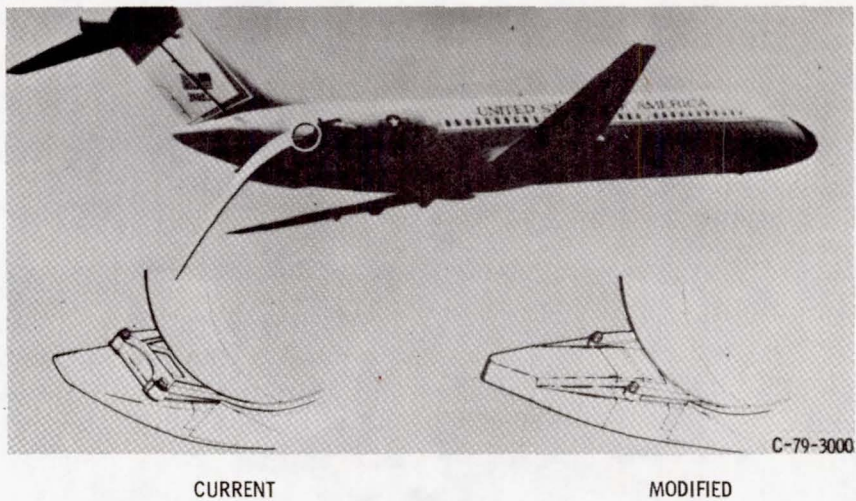


Figure 11. - Douglas DC-9 airplane. Inserts schematically show the current production metal fairing and the redesigned lower drag composite fairing made with Kelvar fabric/PMR-15.

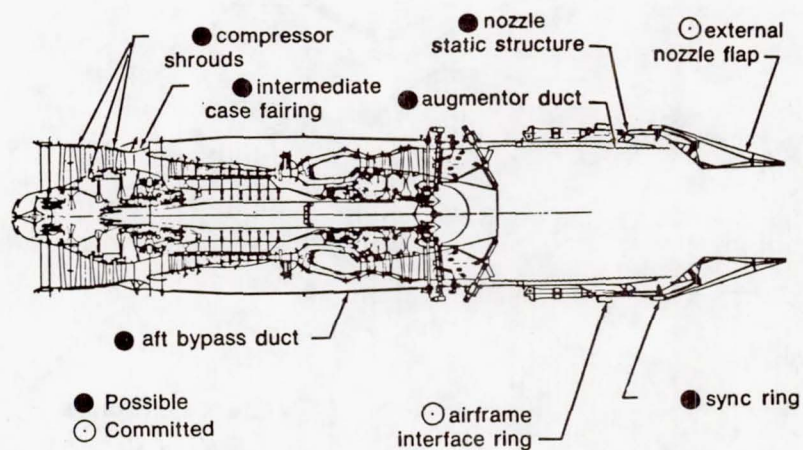


Figure 12. - Schematic of PW1120 showing applications of graphite/PMR-15 materials.

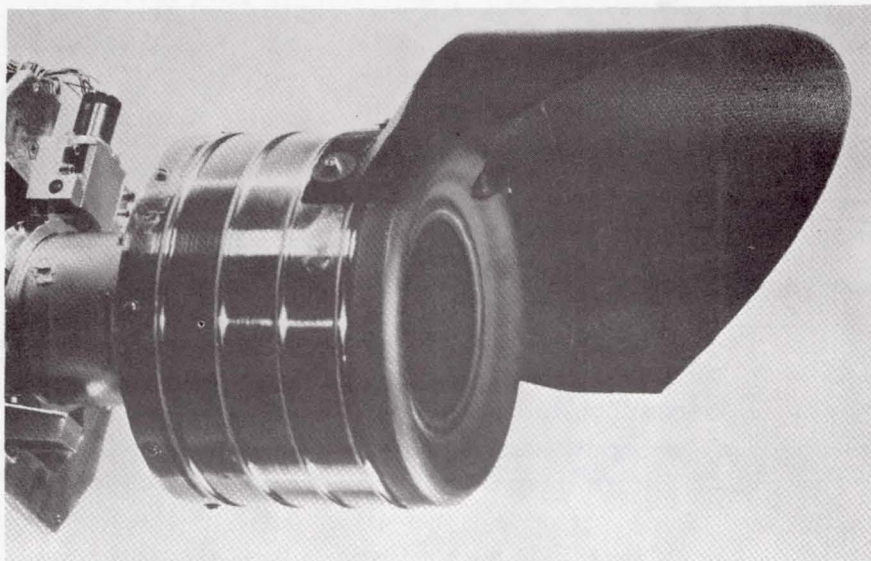


Figure 13. - Mercury ion thruster equipped with glass fabric/PMR-15 beam shield (shield diameter = 10 in.).

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16. Abstract Fiber reinforced PMR polyimides are finding increased acceptance as engineering materials for high performance structural applications. Prepreg materials based on this novel class of highly processable, high temperature resistant polyimides which were first developed at the NASA Lewis Research Center are commercially available and the PMR concept has been adopted by other investigators. This paper reviews the current status of first and second generation PMR polyimides. Emphasis is given to the chemistry, processing and applications of the first generation material known as PMR-15.					
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